Initial Performance of Advanced Designs for IPV Nickel-Hydrogen Cells

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NASA

INITIAL PERFORMANCE OF ADVANCED DESIGNS

FOR IPV NICKEL-HYDROGEN CELLS*

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SUMMARY

Advanced designs for individual pressure vessel nickel-hydrogen cells have been conceived which should improve the cycle life at deep depths-of-discharge and improve thermal management. Features of the designs which are new and not incorporated in either of the contemporary cells (Air Force/Hughes, Comsat) are: (1) use of alternate methods of oxygen recombination, (2) use of serrated edge separators to facilitate movement of gas within the cell while still maintaining required physical contact with the wall wick, and (3) use of an expandable stack to accommodate some of the nickel electrode expansion. The designs also consider electrolyte volume requirements over the life of the cells, and are fully compatible with the Air Force/Hughes design.

Boiler plate cells based on each of the designs have been fabricated. They are in the process of being evaluated in a continuing cycle life test. Initial test results (LEO, 80 percent DOD) demonstrate the feasibility of the designs.

INTRODUCTION

As part of an overall effort to advance the technology of nickel-hydrogen batteries for possible use in an energy storage system, in low earth orbit (LEO), improved advanced designs for individual pressure vessel (IPV) cells have been conceived (Smithrick et al., 1984). The purpose of this effort is to improve the cycle life at deep depths-of-discharge (DOD). The approach has been to effect cell improvements through a continuing combined in-house and contractual effort. Contemporary IPV nickel-hydrogen cell designs and results of cycle life tests conducted in-house and by others were reviewed to identify areas where improvement could results in a longer cycle life. A component improvement effort directed towards the physical properties of each of the individual components was initiated and improvements will be factored into the cell as evolved. Design philosophies have been developed related to oxygen and electrolyte management requirements. Existing technology was utilized where possible to minimize development cost and time.

The contemporary design cells (Air Force/Hughes, Comsat) are adequate for the geosynchronous orbit (GEO) applications, where not many cycles are required

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over the life of the storage system. However, for the demanding LEO applications, the current cycle life at deep depths-of-discharge (2000 to 8000 cycles) is not acceptable (Adler et al., 1980; Warnock, 1982). Some investigators report that this limited cycle life is mainly due to degradation of the nickel electrode (Fritts, 1981 a, b; Pickett et al., 1980). However, several failure mechanisms in IPV nickel-hydrogen cells have been identified which could be eliminated by modification to the SOA cell designs (Smithrick, 1981). These modifications have been incorporated into the NASA advanced design IPV nickel-hydrogen cells.

In this report advanced designs for IPV nickel-hydrogen cells are described. Initial cycle life performance of boiler plate cells, based on each of these designs, is presented and compared to the Air Force recirculating design.

EXPERIMENTAL

Test Facility

The test facility used to cycle life test the nickel hydrogen cells is illustrated in figure 1. The facility design incorporates two main features: safety and versatility. Since the nickel-hydrogen cells are precharged with hydrogen and also generate hydrogen during charge, special attention was given to personnel safety. The cells were located on top of the instrumentation cabinets. There were two cells for each cabinet. Each cell was located within a cylindrical shrapnel shield in case of the improbable event of an explosion or rupture of the cell pressure vessel. During a test, the cylindrical shield was purged with nitrogen to create an inert atmosphere. The nitrogen gas, and hydrogen gas if any, would be exhausted from the test laboratory through a hood located above the cells. If the exhaust fan would fail or the nitrogen purge would become interrupted, the test would be automatically terminated. A test can also be terminated on a present upper and/or lower limit of cell voltage, current pressure, and temperature.

The facility's versatility allows for testing over a wide range of cycle regimes. A geosynchronous earth orbit (GEO) cycle regime can be run in real time using a programmable timer. Various accelerated GEO and low earth orbit cycle regimes can be run using a Texas Instrument timer. The cell discharge current is controlled by an electronic load, which can be varied from 0 to 100 A. The charge current can also be varied in the same range. Test data are printed out locally using a Fluke data collector. Strip chart recorders are used to record cell voltage, current, and pressure as a continuous function of charge and discharge time for selected cycles. A maximum for twelve cells can be tested at the same time.

TEST CELL DESCRIPTION

Air Force Design Cell

The Air Force cell is illustrated in figure 2. It consists of a stack of nickel electrodes, separators, hydrogen electrodes, and gas screens assembled in a non back-to-back electrode configuration. The stack is packaged in a cylindrical pressure vessel, with hemispherical end caps. This is made of

Inconnel 718 and lined with zirconium oxide which serves as a wall wick. The components are shaped in a "pineapple" slice pattern. The electrodes are connected electrically in parallel. In this configuration electrodes of different types directly face each other. Hence, since a high bubble pressure separator is used, the oxygen generated at the nickel electrode on charge is directed to the hydrogen electrode of the next unit cell, where it recombines chemically to form water. The fuel cell grade asbestos separators are extended beyond the electrodes to contact the wall wick. Hence, electrolyte which leaves the stack during cycling will be wicked back into the stack. The nickel electrode consists of a sintered nickel powder plaque containing a nickel screen substrate which is electrochemically impregnated with nickel hydroxide active material by the Pickett process. The gas screens are polypropylene. The electrolyte is a 31 percent aqueous solution of potassium hydroxide. The stack configuration is referred to as a recirculating design.

NASA ADVANCED CELLS

Overall Design

Two different but similar advanced design IPV nickel-hydrogen cells have been conceived. They are illustrated in figures 3 and 4. One is referred to as the catalyzed wall wick and the other as the oxygen recombination capsule design. Initially the nickel electrodes, hydrogen electrodes, gas screens, pressure vessel, and potassium hydroxide electrolyte concentration will be identical to the ones used in the state-of-the-art Air Force/Hughes cells. However, a component improvement effort directed towards the physical properties of each of the individual components has been initiated and improvements will be factored into the cells as they evolve. For both designs the electrode configuration is back-to-back as is the case for the Comsat cell. Both designs also use a wall wick, however portions of the wall wick are catalyzed for the catalyzed wall wick design.

Features of the advanced designs which are new and not incorporated in either of the contemporary cells are: (1) use of alternate methods of oxygen recombination; (2) use of serrated edge separators; and (3) use of an expandable stack. The designs also consider electrolyte volume requirements over the life of the cells, and are fully compatible with the Air Force/Hughes design.

Boiler plate cells of both designs are in the process of being cycle tested to verify design feasibility.

Oxygen Management

During the later part of charge and on overcharge oxygen is evolved at the nickel electrodes. For both contemporary designs oxygen management consists of chemically recombining the oxygen generated during charge on catalyzed hydrogen electrode surface to form water. This chemical reaction is very exothermic; hence care must be taken to limit the rate at which these two reactants come together. If a separator is used which has a pore size distribution that permits a certain degree of gas permeability, oxygen bubble buildup occurs and "popping" results as these accumulations of oxygen abruptly recombine. This can result in sintering of the catalyzed surface and/or local melting of

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the Teflon/catalyzed agglomeration that makes up the hydrogen electrode. If high bubble pressure separators are used in the back-to-back electrode configuration (Comsat design) the oxygen must travel along the face of the nickel, leave the stack, and then reenter to recombine on the hydrogen electrode. In this case, the recombination would be expected to take place around the outer perimeter of the electrodes. The concentration of chemical reactants could result in damage to the electrocatalyst surface of the electrode.

An improved method of oxygen recombination is to use a catalyzed wall wick. The oxygen evolved on charge between the back-to-back nickel electrodes is directed to the catalyzed wall wick where it recombines. The water formed is wicked into the stack because the asbestos separators are in contact with the wall wick. An oxygen seal is used at the inner edge of the nickel electrodes to preclude oxygen from bypassing the catalyzed wall wick by escaping into the stack core, and reentering to recombine at the hydrogen electrodes. The asbestos separator pore size distribution is such that it has a high bubble pressure, thus denying the oxygen a direct path to the hydrogen electrode.

The catalyzed wall wick is fabricated by first depositing a thin zirconium oxide layer of wicking material on the inner surface of the pressure vessel, as is the case in the Air Force design. A platinum Teflon mixture is coated in stripes onto the zirconium oxide surface. The mixture is similar to that used to fabricate SOA hydrogen electrodes, and is cured in the same manner.

The advantages of using a catalyzed wall wick are: (1) aids thermal management, as the heat of oxygen recombination is deposited at the pressure vessel wall rather than at the hydrogen electrodes in the stack, and (2) prevents damage to the hydrogen electrode due to concentrated bubbles of oxygen reacting (popping problem).

Another method of oxygen management would be to use oxygen recombination capsules between the back-to-back nickel electrodes. The high bubble pressure asbestos separator directs the oxygen into the capsule, which consists of recombination sites catalyzed with platinum. They are encapsulated with a vapor permeable coating to allow passage of the gases in and water vapor out, but remain hydrophobic to liquid. The coating must also isolate the catalyst electrically, otherwise it will react with the nickel electrode as a parasitic reaction. The water formed within the capsule is returned to the nickel electrodes in the vapor form. This method of oxygen management benefits the overall electrolyte management scheme, and helps prevent damage to the hydrogen electrode.

Expandable Stack

The SOA electrochemically impregnated nickel electrodes expand significantly due to cycling at deep depths-of-discharge compressing the separators. The electrolyte forced out is absorbed by the increased pore volume of the nickel electrodes. Hence, expansion of the nickel electrodes effects electrolyte volume (as a percentage of stack saturation) and electrolyte distribution. This failure mode applies to the Comsat cell, which does not use a recirculation stack. In the Air Force cell, the proper electrolyte volume should be maintained by the recirculation stack design. However, it has been reported by others that the Air Force cell has also failed due to nickel electrode expansion (Muller, 1984). In this case, the expansion was so great (about

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1/2 in., 40 electrode stack) that the polysulfone core of the stack ruptured. This failure mode can be eliminated by modifying the cell design to accommodate expansion.

To accommodate the nickel electrode expansion and improve cycle life, an expandable stack has been proposed. One way of implementing this is to use Incomel 718 Belleville disc springs at each end of the stack between the end plates and tie rod nuts. The springs will maintain stack compression throughout the life of the cell and also accommodate expansion. Another way is to share the accommodation with the separator. The spring constant can be selected so that some of the electrode expansion is absorbed by the asbestos separator. A 10 mil separator, which is the standard thickness used in contemporary nickel-hydrogen cells, can be compressed to about 5 mil without any performance degradation provided it has adequate electrolyte. In SOA cells, the asbestos separators are initially compressed 1 mil to insure good component contact. As a matter of fact, the performance of the separator may improve due to the decrease in thickness. However, this could be offset by a change in tortuosity due to compression. The separator can be thought of as a spring in series with the Belleville spring. The relative deflection will depend on the respective spring constants.

An effort has been initiated in-house to investigate the effect of separator compression on resistance and electrolyte content.

Serrated Separator

The separators are made of beater treated asbestos (BTA) rather than conventional fuel cell grade asbestos. BTA is reconstituted fuel cell grade asbestos that has 5 percent by weight butyl latex binder added (Schmidt et al., 1981). The sheet is formed in 1 ply and is approximately 7 mil thick. The properties of BTA are comparable to those of the fuel cell grade asbestos (resitivity, electrolyte retention, porosity, pore size, and bubble pressure). In addition, the BTA is more uniform and stronger. The edges of the separator are serrated to facilitate gas movement inside the cell. The duty cycle of the serration is about 25 percent. Hence, 75 percent of the separator edge will still be in contact with the pressure vessel wall for electrolyte management.

Electrolyte Management

Cell performance is very sensitive to stack electrolyte volume distribution (Abbey et al., 1982). There are many factors which effect this quantity, and some are difficult to control. However, by good design, proper electrolyte volume can be maintained over the life of the cell for good performance.

One way of maintaining the proper electrolyte volume is to provide extra electrolyte in the bottom of the cell (about 20 mil) and a means of transporting it to the stack as required. This can be done by extending the separators beyond the electrodes to contact the wall wick, which is in contact with the electrolyte reservoir, as is the case in the Air Force design.

MEASUREMENTS AND PROCEDURE

For this experiment the quantities measured for each cell at the end of charge and discharge, and their accuracies were: current (±0.3 percent), voltage (±0.5 percent), pressure (±1 percent), temperature (±1 °C limit of error), and charge and discharge ampere-hours capacity (±0.5 percent). Charge-to-discharge ampere-hour ratio was calculated. Cell current, voltage, and pressure were recorded continuously as a function of time, for selected cycles, on a strip chart recorder.

Cell charge and discharge currents were measured across a shunt, using an integrating digital voltmeter. Cell voltage was also measured using an integrating digital voltmeter. Cell pressure was measured using a conventional pressure transducer. Temperature was measured using an iron-constantan thermocouple located on the center of the outside pressure vessel wall. Charge and discharge ampere-hours were measured using a conventional ampere-hour meter. Charge-to-discharge ratio (ampere-hours into cell on charge to ampere-hours out on discharge) was calculated from the ampere-hour measurements.

Prior to cycling the cell, the ampere-hour capacity loss due to self discharge after a 72 hr open circuit voltage stand was measured for all cells.

Three, 6 Ah boiler plate cells of each design will be cycled to failure. The cycle regime will be a LEO regime. The depth-of-discharge will be 80 percent of name plate capacity. For this test cell failure was defined to occur, when the discharge voltage degraded to 0.9 V during the course of a constant current 35 minute discharge at the 1.37 C rate. For the first test cycle, the cells were charged for 18 hr at a C/10 rate (0.6A) followed by discharge at the 1.37 C rate for 35 min. Then the normal LEO charge/discharge regime was initiated which consisted of charging the cells at about a constant 0.96 C rate (5.76 A) for 55 minutes immediately followed by discharge at a constant 1.37 C rate (8.2 A) for 35 min. The charge-to-discharge ratio was set at 1.10.

RESULTS AND DISCUSSION

Self Discharge

The average percentage ampere-hour capacity loss and confidence interval (standard deviation about the mean) for three cells of each design is summarized in figure 5. The capacity loss was measured after a 72 hr open circuit voltage stand. The cell temperature was not controlled during the measurements. Room temperature was 25 °C. The spread in the data indicates no significant difference in the average percentage capacity loss. This suggests that the new designs do not introduce any new self discharge mechanisms.

Cycle Performance

The effect of cycling on the end of discharge voltage for the best cell of each design is shown in figure 6. There is no apparent difference between the performance of the oxygen recombination capsule cell and the Air Force control cell. The voltage for both designs was stable and relatively constant throughout the test except after a capacity measurement where the performance

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improved for both designs. At cycle 3600 the end of discharge voltage is about 1.14 V for each design cell. The catalyzed wall wick cell initially exhibited a lower than expected end of discharge voltage. One possible cause for this low voltage could be inadequate electrolyte. To verify this, the cell was taken off test at cycle 200, vacuum filled with electrolyte, and stored at open circuit voltage for 20 days. After the open circuit voltage stand the cell was placed back on test. The effect of vacuum filling with electrolyte on the cell performance was dramatic. The end of discharge voltage increased from 0.82 to 1.17 V. The voltage leveled off at about 1.14 V and remained relatively constant. At cycle 2000 the voltage remains at about 1.14 V. Hence after vacuum filling with electrolyte there is no apparent difference between the performance of the catalyzed wall wick cell and the Air Force control cell.

The cycle test of these cells will be continued until failure. A post-cycle cell teardown and failure analysis will be conducted to evaluate the cause(s) for failure. This information will be used to further improve the cell designs.

CONCLUDING REMARKS

Advanced designs for IPV nickel-hydrogen have been conceived, which could have a longer cycle life at deep depths-of-discharge and improved thermal management. The features of the designs which are new are: use of alternate methods of oxygen recombinations, use of an expandable stack to accommodate nickel electrode expansion, and use of serrated edge separators to facilitate gas movement within the cell while still maintaining required physical contact with the wall wick. The designs also consider electrolyte volume requirements over the life of the cells, and are fully compatible with the Air Force/Hughes design.

Boiler plate cells based on each of the designs have been fabricated and are in the process of being evaluated in a continuing cycle life test. Initial results indicate the feasibility of the design.

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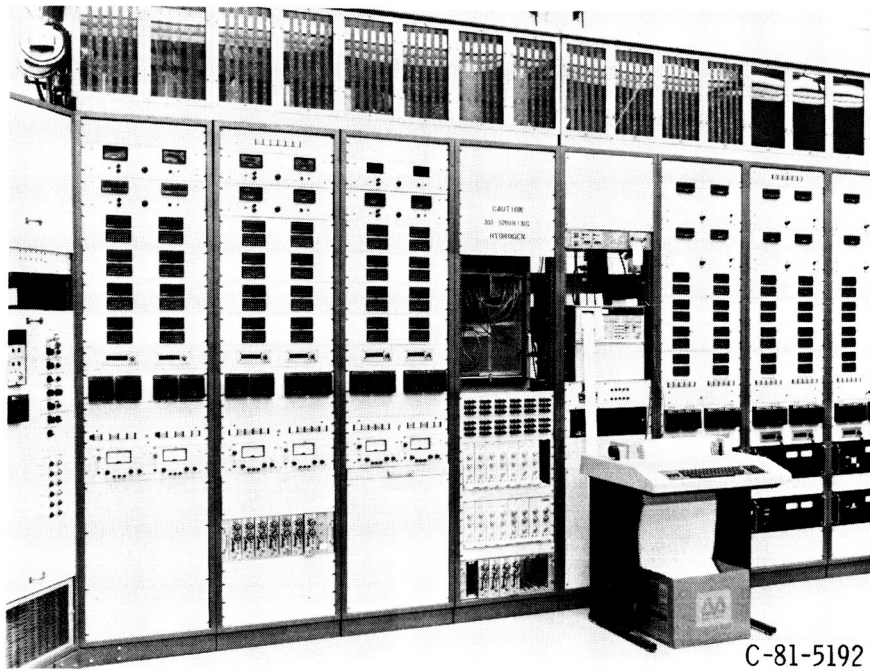
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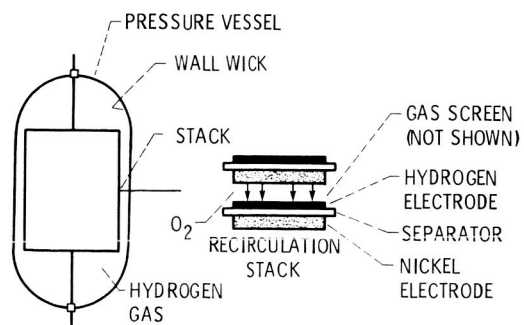
Figure 1. - Nickel-hydrogen cell test facility.

Figure 2. - Illustration of Air Force/Hughes design individual
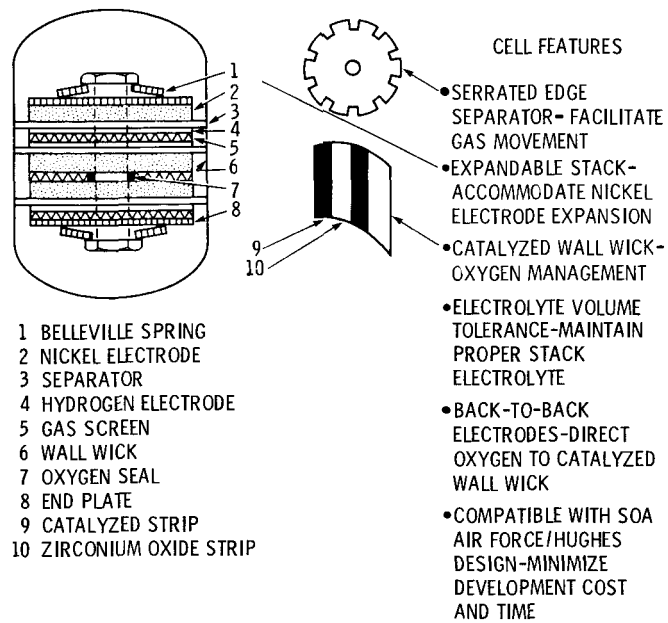pressure vessel nickel-hydrogen cell.

CELL FEATURES

•SERRATED EDGE
SEPARATOR- FACILITATE
GAS MOVEMENT

•EXPANDABLE STACK-
ACCOMMODATE NICKEL
ELECTRODE EXPANSION

•CATALYZED WALL WICK-
OXYGEN MANAGEMENT

•ELECTROLYTE VOLUME
TOLERANCE-MAINTAIN
PROPER STACK
ELECTROLYTE

•BACK-TO-BACK
ELECTRODES-DIRECT
OXYGEN TO CATALYZED
WALL WICK

•COMPATIBLE WITH SOA
AIR FORCE/HUGHES
DESIGN-MINIMIZE
DEVELOPMENT COST
AND TIME

1 BELLEVILLE SPRING
2 NICKEL ELECTRODE
3 SEPARATOR
4 HYDROGEN ELECTRODE
5 GAS SCREEN
6 WALL WICK
7 OXYGEN SEAL
8 END PLATE
9 CATALYZED STRIP
10 ZIRCONIUM OXIDE STRIP

Figure 3. - NASA advanced design IPV nickel-hydrogen cell-catalyzed wall wick.

1 NICKEL ELECTRODE
2 OXYGEN RECOMBINATION UNIT
3 GAS SCREEN - POLYPROPYLENE
4 SEPARATOR - BEATER TREATED ASBESTOS
5 HYDROGEN ELECTRODE
6 ELECTRICAL LEADS
7 PRESSURE VESSEL
8 BELLEVILLE SPRING
9 WALL WICK
10 STACK
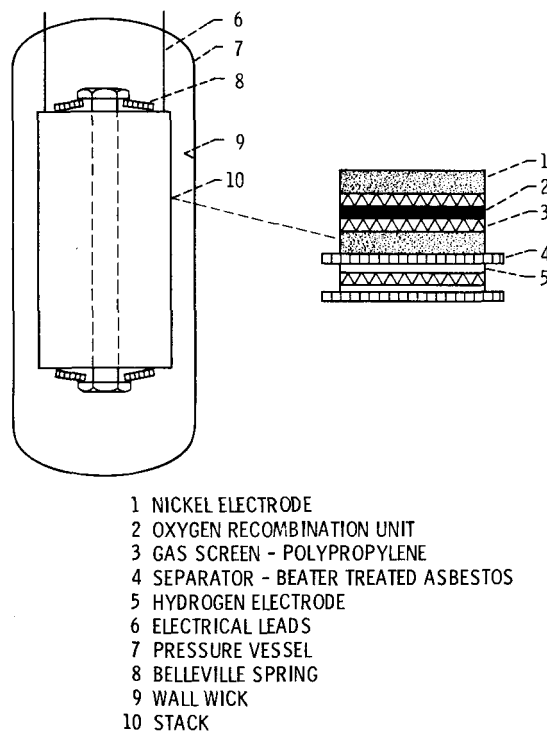
Figure 4. - NASA advanced design nickel-hydrogen cell - oxygen recombination capsule.

CELL DESIGN

AIR FORCE

OXYGEN RECOMBINATION CAPSULE

CATALYZED WALL WICK

| | | | | | | | | | | |
0   4   8   12 16 20 24 28 32 36 40
AMPERE-HOUR CAPACITY LOSS, PERCENTAGE
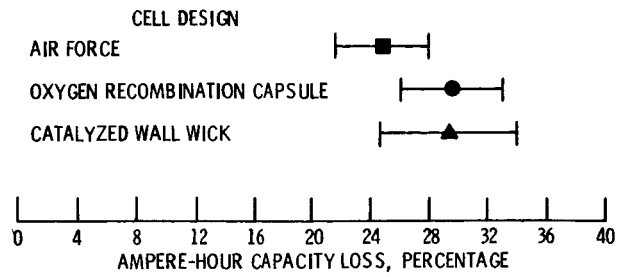
Figure 5. - Self discharge - average capacity loss and confidence inter-
val after 72 hr open circuit voltage stand.

CELL DESIGN

○ OXYGEN RECOMBINATION CAPSULE
△ CATALYZED WALL WICK
□ AIR FORCE

1 PERFORMANCE AFTER ELECTROLYTE REFILL
2 PERFORMANCE AFTER CAPACITY MEASUREMENT
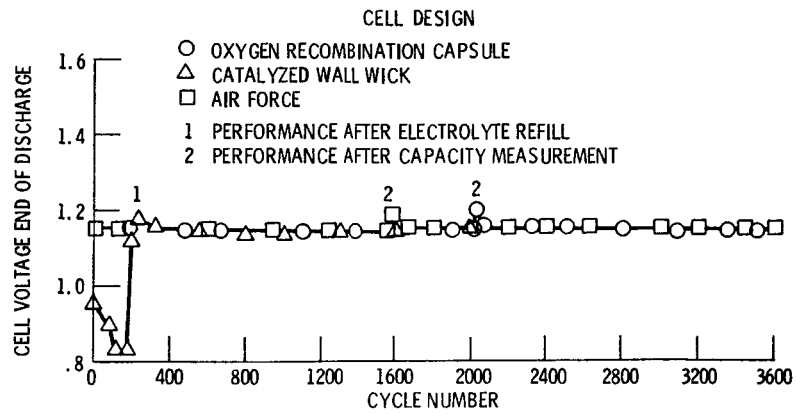
CELL VOLTAGE END OF DISCHARGE

Figure 6. - Effect of cycling on end of discharge voltage of best cell of each design.

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16. Abstract

Advanced designs for individual pressure vessel nickel-hydrogen cells have been conceived which should improve the cycle life at deep depths-of-discharge and improve thermal management. Features of the designs which are new and not incorporated in either of the contemporary cells (Air Force/Hughes, Comsat) are: (1) use of alternate methods of oxygen recombination, (2) use of serrated edge separators to facilitate movement of gas within the cell while still maintaining required physical contact with the wall wick, and (3) use of an expandable stack to accommodate some of the nickel electrode expansion. The designs also consider electrolyte volume requirements over the life of the cells, and are fully compatible with the Air Force/Hughes design.

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